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BURNING CHARACTERISTICS AND FIBER
RETENTION OF GRAPHITE/RESIN
MATRIX COMPOSITES

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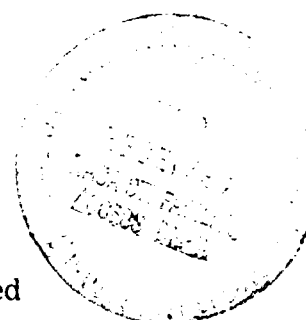
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BURNING CHARACTERISTICS AND FIBER RETENTION OF GRAPHITE/RESIN MATRIX COMPOSITES

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ABSTRACT

Graphite fiber reinforced resin matrix composites were subjected to controlled burning conditions to determine their burning characteristics and fiber retention properties. Two types of burning equipment were used. Small samples were burned with a natural gas fired torch to study the effects of fiber orientation and structural flaws such as holes and slits that were machined into the laminates. Larger laminate samples were burned in a modified Ohio State University Heat Release Rate Calorimeter. Unidirectional epoxy/graphite and polyimide/graphite composites and boron powder filled samples of each of the two composite systems were burn tested. The composites were exposed to a thermal radiation of $5.3 \text{ Btu/ft}^2\text{-sec}$ in air. Samples of each of the unfilled composites were decomposed anaerobically in the calorimeter. Weight loss data were recorded for burning and decomposition times up to thirty-five minutes. The effects of fiber orientation, flaws, and boron filler additives to the resins were evaluated.

A high char forming polyimide resin proved to be no more effective in retaining graphite fibers than a low char forming epoxy resin when burning was done in air. Boron powder additions to both the polyimide and the epoxy resins stabilized the chars and effectively controlled the fiber release.

INTRODUCTION

The potential hazards associated with the release of free floating graphite fibers from burning composite materials are described in references 1, 2, and 3. A description of fiber release testing programs and some results from these tests are presented in reference 4.

In addition to the programs in which tests were conducted to quantify the fiber release characteristics of various types of resin matrix composites, a number of programs are now in progress to produce composites which retain the graphite fibers when subjected to burning conditions. Some of the concepts being studied are hybridized reinforcement, mechanical containment by stitching or non-consumable surface plies, fiber modification, resin modification, and the use of particulate fillers.

The purpose of this paper is to describe an investigation of the release of graphite fibers from burning graphite reinforced, resin matrix composites. Initially, work was directed toward establishment of a reference system of composite structures which would allow fiber release characteristics to be observed. Then the effects of selected variables

such as time, char formation, and resin filler on the observed fiber release were determined. Small graphite reinforced composite samples were burned in a natural gas fired torch burning apparatus. The results of this small scale testing were used to develop a simplified approach to study the effects of resin char formation and resin filler material on graphite fiber release from burning composites. Using this approach, larger samples of graphite/resin and graphite/resin/filler composite laminates were burned in an Ohio State Heat Release Rate (OSU-HRR) Calorimeter (Ref. 5). Weight losses and char formation were measured. Fiber release characteristics as well as fiber degradation were assessed.

MATERIALS

Two resin/graphite systems were included in this study. One system contains a relatively high char forming resin designated as PMR-15. This is a polyimide resin formed from the monomeric reactants (1) 4,4'-methylenedianiline, (2) monomethyl ester of 5-norbornene-2,3 dicarboxylic acid, and (3) dimethyl ester of 3,3',4,4' benzophenonetetracarboxylic acid. The solvent used was methyl alcohol. The solution was prepared according to the procedure reported in reference 6.

The graphite fiber used for this study was Hercules HTS-II (HTS). The fiber was drum wound at a pitch of seven turns per inch and was impregnated with the PMR-15 polyimide solution. The solution had a solids content of 50% by weight. Heat lamps were used to reduce the solvent content to about 10% before the prepreg was removed from the drum. Unidirectional plies were cut from the prepreg. These plies measured 3 inches by 10 inches with the fiber direction parallel to the 10 inch direction. Nine plies were stacked together; and then they were imidized, cured, and postcured as described in reference 6. The laminate thicknesses ranged from 0.090 to 0.125 inches.

The other resin chosen was a low charring epoxy resin, designated Hercules 3501-6 (3501-6). This epoxy resin cures at 350°F and contains N,N,N',N' tetraglycidyl methylenedianiline and an aromatic curing agent. The resin was prepared as an 80% by weight solution in methyl ethyl ketone.

HTS-II graphite fiber was also used as the reinforcing material for the epoxy matrix laminates. The epoxy laminates were made by winding seven turns per inch of the HTS fiber on a drum and impregnating the fiber with the 3501-6/methyl ethyl ketone solution. The impregnated fibers were air dried to a slightly tacky condition and then removed from the drum. Nine 3 inch by 10 inch plies were stacked to form one laminate. The laminates were unidirectional with the fiber direction parallel to the 10 inch direction of the plies. Each stack of plies was heated to 230°F in an air circulating oven for one hour. The individual stacks were then allowed to cool, placed in a matched metal die mold and heated under contact pressure to 350°F. A pressure of 200 psi was applied to the laminate at a temperature of about 280°F or when the resin flash started gelling. The laminate was then held under pressure at 350°F for one hour. After the laminate had cooled and was removed from the mold, it was postcured for two hours at a temperature of 400°F in air. The range of thicknesses for the epoxy laminates was from 0.070 to 0.100 inches.

The boron powder filler material used in this study had a particle size of $44\mu\text{m}$ (-325 mesh) and a purity of 95%. When boron fillers were added to the laminates, they were first mixed with the resin solution and then applied as a suspension in the resin solution to the graphite fibers.

The amount of boron powder added to the resins equaled 10% of the fiber weight for the epoxy prepreg and 17% of the fiber weight for the polyimide prepreg. These levels of boron content were shown to be effective in preliminary fiber retention studies (Ref. 7).

EQUIPMENT

Preliminary work was conducted using a Pyrex tube gas burner. This apparatus is shown in Figure 1. It is a Pyrex tube with a stainless steel cap on the top. The cap has an opening which connects to a vacuum cleaner hose. A vacuum cleaner is used to pull air through the tube. A fiberglass cloth filter in the line collects any fibers which may be released from the sample. The sample is positioned at the bottom of the tube and is burned by a natural gas/air flame. The tube test sample and burner are contained within a stainless steel base assembly which is used to collect any debris which might fall from the sample as it burns. The flame temperature and sample surface temperatures were measured with chromel-alumel thermocouples.

Burning tests of the larger composite samples were conducted in the Ohio State University Heat Release Rate (OSU-HRR) Calorimeter. The apparatus as described in reference 5 has been modified as shown in Figure 2.

TEST PROCEDURE

In testing resin matrix graphite reinforced composites for fiber release characteristics, various types of composite designs were screened. Some of these were hybridized fiber composites, glass fabric covered composites and composites coated with various materials. They all exhibited different behavior to the burning environment. Because of the difference in reactions, no means of comparative evaluation could be established. The burning process was too complex, with regard to the reactions of different materials and different ply orientations to sudden thermal gradients, high temperatures, and thermal degradation. Significant amounts of released graphite fiber were not readily obtained in many cases even though significant amounts of free graphite fibers were present on the surfaces of the samples. Because of this complexity, a simplified unidirectional fiber oriented composite design was chosen for study even though it was not representative of a functional structural composite design.

For those tests which were run in the Pyrex tube chamber, a fiberglass cloth filter was installed in the outlet to the vacuum cleaner and the vacuum cleaner was turned on. The burner was lit and the flowmeters in the natural gas and air lines were adjusted to produce a flame temperature of 2100°F . The 0.5 inch by 3 inch sample was then positioned in the flame and burning was allowed to proceed for the desired period of time. The burner was then turned off. Burning times ranged from five to fifteen minutes.

All samples burned in the OSU-HRR Calorimeter measured 3 inches by 6 inches. A total air flow rate of 85 cubic feet per minute was metered through the OSU-HRR Calorimeter. Of this amount, 21 cubic feet per minute actually flowed through the burning chamber and past the laminate being tested. The remaining air flowed through the top end of the Calorimeter. The gas pilot was lit and the gas flow was adjusted through a flowmeter to a flow of 2 cubic feet per hour. The radiant heaters were energized and the apparatus was allowed to reach thermal equilibrium. The heater current was then adjusted to produce the desired radiation value. The radiation energy was measured with a radiometer. The samples were inserted into the Calorimeter and allowed to burn for the required amount of time. The heat release rate and the smoke release rates were recorded on a two pen recorder. At the end of the predetermined exposure time, the sample was removed from the burning chamber.

Each of the laminates was burned in the OSU-HRR Calorimeter for five minutes and then removed and weighed. Each laminate was then placed back into the Calorimeter for an additional 10 minutes. The sample was then removed and again weighed. If the laminate retained enough resin char so that it could be easily handled, it was then reinstalled in the burning chamber for an additional 20 minutes and then removed and weighed.

Char characteristics were assessed based on resin weight loss. Fiber retention characteristics were based on the presence of free fibers on the sample surfaces and also on the thermo-oxidative stability of the resin char formed during the burning tests.

When a composite laminate sample was to be decomposed anaerobically in the OSU-HRR Calorimeter, the air line to the burning chamber was closed with a valve. The air flow through the top of the Calorimeter was maintained at a rate of 64 cubic feet per minute and a nitrogen flow of 21 cubic feet per minute was directed through the burning chamber.

RESULTS AND DISCUSSION

Small Scale Tests

From the work done in the Pyrex tube burning apparatus, some general observations were made which were important in clarifying and isolating some of the significant factors which influenced the small scale burning tests.

Fiber retention during burning was found to be very sensitive to the fiber orientation in the test specimen. Figure 3 illustrates three test specimens with three different fiber orientations. The figure shows samples with fibers oriented parallel to the long dimension, at an angle of 45° to the long dimension and perpendicular to the 3 inch dimension. The flame affected areas of the samples are outlined by the circles which represent the impinging flame from the burner. Depending on the orientation of the reinforcement fibers during the burning tests, the fiber release steadily increased as the orientation angle increased from 0° to the 3 inch dimension to an angle of 90° . The force of the impingement of the flame on the burning sample caused the free fibers to be removed as soon as they were formed.

The initial results in the Pyrex burning apparatus indicated that the quantities of released fibers was strongly dependent on fiber orientation. Only a small portion of the 0° fibers were exposed by the burning, and they were restrained from floating free by the unburned resin at the ends of the samples. The fibers oriented 90° to the long direction of the sample were completely free from unburned resin and from char and some fibers floated free.

Another series of tests was performed with the Pyrex tube gas burner using unidirectional specimens with machined defects. The defects were in the form of holes, slits through the entire thickness of the samples, and surface cuts penetrating to about one-half the thickness of the samples. The cuts and slices were machined to cut across the reinforcing fibers. These machined defects were introduced to represent fastener holes, and cracks. The sample geometry effect observed with these small samples was reduced by the presence of the artificial defects. The defects increased the release of fibers and the release was found to be independent of the orientation of the fibers with respect to the sample dimensions.

The results of these series of small scale tests provided guidelines for the remainder of the work. Unidirectional laminates with 0° fiber orientation were chosen for further testing. The criterion for evaluating the effectiveness of resins or composite modifications on fiber retention was based on the presence of free fibers exposed by the burning tests. If the exposure to an extreme thermal environment produced bare graphite fibers, these fibers could be dislodged from the remainder of the burned composite by a variety of circumstances. This applied only to those composites which were being tested to observe the effectiveness of the resin char or the resin and filler residue in increasing fiber retention. This criterion probably does not apply to those composite systems designed to use mechanical means for retaining graphite fibers.

One other observation was noted from the tests which were conducted in the Pyrex tube burner. When the epoxy composite started burning, a surface flame was initiated which spread rapidly and eventually covered the entire surface of the sample. The surface flame lasted for about one minute and then the burning was confined to the area exposed to the burner flame. In contrast, the PMR-15 matrix specimen burned with the surface flame confined to that portion of the surface which was in direct contact with the burner flame. The significance of this observation is that with this type of test the amount of sample involvement varies with the type of resin used. Because of this, it is difficult to evaluate weight loss data by direct comparison between different samples. Therefore, testing procedures for the remainder of this study were designed to include the exposure of the entire sample surface to a uniform burning environment.

OSU-HRR Calorimeter Tests

The Ohio State Heat Release Rate Calorimeter was chosen as the testing apparatus for the more controlled burning test. This test provides a reproducible environment and the heat flux to which the samples are exposed can be readily measured. It also provides heat and smoke release

data which, although not a requirement for fiber release studies, does provide a means for better understanding the burning process both in general and for individual composite systems. The equipment can easily be adapted to allow loose fiber collection. Also, this equipment allows the opportunity for a clear visual observation to be made during each burning test.

For the simple graphite/resin fiber composites tested in this work, the only method of fiber retention which can be expected is that in which the solid combustion products (the char or char and additive material) are oxidatively stable under the burning test conditions and adhere to the fibers so that free fibers will not be exposed.

The boron filled laminates and the unfilled laminates were burned in air. The unfilled laminates were anaerobically decomposed in nitrogen. The anaerobic conditions were chosen to provide a baseline value for char formation for each composite system against which the air burning characteristics could be compared.

The results of the burning tests are presented in Table I and Table II. Table I gives weight loss data for the laminates that were burned in air. Weight loss data are presented both as percent laminate weight loss and as percent resin weight loss. The resin weight loss data are also plotted in Figure 4. Figure 5 is representative of the difference in surface appearance between an unfilled epoxy laminate burned in air and a boron filled epoxy sample burned in air. The total burning time for both panels was 35 minutes. Both the unfilled polyimide and epoxy laminates were reduced to piles of free graphite fiber after the burning tests were concluded. All boron filled samples exhibited solid almost shiny surfaces with no visible free fibers present.

From the data in Table I and Figure 4, it is evident that significant fiber loss occurred in the unfilled laminates. Fiber accumulation was not found in the filtering system. It is assumed that this weight loss is dependent on the amount of free graphite fibers and the major loss of weight occurred during the period after surface burning has ceased (after the first three to five minutes of testing). The percent resin loss data for the two unfilled samples burned in air are artificially large because they include a significant amount of fiber weight loss after five minutes.

The boron filler appeared to stabilize the char after the first five minutes of burning. This stabilization is probably associated with the formation of low melting oxides of boron that tend to protect the resin-char from further oxidation. The lower resin weight loss value for the unfilled epoxy laminate during the first eight minutes of burning compared with the boron-filled laminate as shown in Figure 4 may be due to the manner in which the boron content and the resin content of the as-fabricated boron-filled laminates were calculated. The fiber weight was determined using the acid digestion method described in reference 8. Using this method it was not possible to measure the actual boron content. Therefore, it was assumed that the as-fabricated resin/boron weight ratio was the same as the resin/boron weight ratio in the prepreg. However, it may be possible that during processing, the resin and particulate boron flowed at different rates, resulting in a different resin/boron weight ratio.

Table II and Figure 6 show the data from the anaerobic decomposition of the unfilled epoxy and the unfilled polyimide laminates. Also plotted in Figure 6 are the data from the burning tests of the corresponding boron-filled systems in air. The resin loss values from the anaerobic decomposition of the polyimide laminate and the boron-filled polyimide laminate burned in air are in close agreement. The char residue in the boron-filled epoxy laminate that was burned in air is about one-half the amount present in the unfilled epoxy laminate decomposed in nitrogen. Figure 6 shows 66% resin weight loss for the anaerobic decomposition of the unfilled epoxy laminate and 84% resin weight loss for the air burned boron filled epoxy laminate. This is significantly different from the char formation characteristics of the polyimide-boron mixture. The reason for this difference in behavior is not apparent, however, it may be due to the smaller amount of char produced by the epoxy resin. While the maximum amount of epoxy-boron char (based on anaerobic tests) was not retained in the burned graphite/epoxy laminate, the laminate did not contain any loose graphite surface fibers and no fibers were collected in the filter system. The fiber retention properties of the filled laminates were excellent.

In the work described above, the boron weight fraction of the polyimide laminate was 0.10. The boron weight fraction of the epoxy laminate was .041. These are calculated contents. Some short time burning test data were obtained early in this study to determine if the difference in boron content had an effect on char formation. One HTS/PMR-15 and one HTS/PMR-15/B laminate were burned in the OSU-HRR Calorimeter at the Ohio State University under the same conditions as the laminates burned in the long time tests. The boron weight fraction of the filled sample was calculated to be .049. The calculated resin loss for the boron filled sample was 36.8% and the calculated resin weight loss for the unfilled laminate was 54.5%. Both samples were burned for 5.5 minutes. These data are in good agreement with the resin weight loss data from Table I. This indicates that for the polyimide matrix graphite fiber reinforced composites, this difference in filler weight content did not affect the char formation value significantly.

SUMMARY OF RESULTS

1. Fiber release is very sensitive to fiber orientation when burning small samples of thin, unidirectional, graphite fiber reinforced resin matrix composites in air. Fiber release increases as the fiber orientation relative to the length increases from 0° to 90° . Defects reduce the sensitivity of fiber release to fiber orientation for small samples.
2. After prolonged burning of thin unidirectional graphite fiber reinforced resin matrix composites in air, neither high char forming polyimide resins nor low char forming epoxy resins effectively retain the graphite fibers.
3. The addition of boron powder to thin, unidirectional PMR-15/HTS composites stabilizes the char formed from burning in air. The char formation characteristics in air appear to be identical with the char

forming characteristics of anaerobically decomposed HTS/PMR-15 composites. It also appears that there is no significant effect of boron content on the char forming characteristics of this material in the weight percent range of 5% to 10%. The char formed effectively prevents release of graphite fibers.

4. The addition of boron powder to thin, unidirectional HTS/3501-6 composites, effectively stabilizes the char formed from burning in air. The char which is formed is effective in preventing graphite fiber release from the burned material. The char forming characteristics in air appear to be similar to the char forming characteristics observed after anaerobically decomposing HTS/3501-6. However, the amount of char formed was only half as much as the char formed from anaerobic decomposition of this composite system.

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TABLE I. - WEIGHT LOSS OF HTS/EPOXY AND HTS/POLYIMIDE RESIN MATRIX LAMINATES
EXPOSED TO A THERMAL RADIATION OF 5.3 BTU/FT.²-SEC IN AIR

Composite	Weight % Resin As Fabricated	% Laminate Weight Loss			% Resin Weight Loss		
		5 Min.	15 Min.	35 Min.	5 Min.	15 Min.	35 Min.
HTS/3501-6	24.2	18.0	21.9	*	74.3	90.4	*
HTS/3501-6/B	27.0	21.8	22.8	22.6	80.5	84.3	83.8
HTS/PMR-15	38.3	18.0	29.7	50.5	47.9	77.6	132.0
HTS/PMR-15/B	34.7	11.3	12.4	11.3	32.5	35.6	32.6

*All loose fibers. Could not be reinserted for 35 minute test.

TABLE II. - WEIGHT LOSS OF HTS/EPOXY AND HTS/POLYIMIDE MATRIX LAMINATES
EXPOSED TO A THERMAL RADIATION OF 5.3 BTU/FT.²-SEC IN NITROGEN

Composite	Weight % Resin As Fabricated	% Laminate Weight Loss			% Resin Weight Loss		
		5 Min.	15 Min.	35 Min.	5 Min.	15 Min.	35 Min.
HTS/3501-6	26.8	17.9	17.7	17.9	66.6	65.8	66.6
HTS/PMR-15	40.1	15.5	16.3	14.1	38.6	40.6	35.3

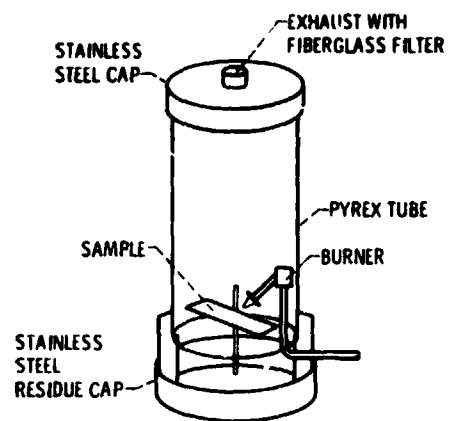


Figure 1. - Pyrex tube gas burner.

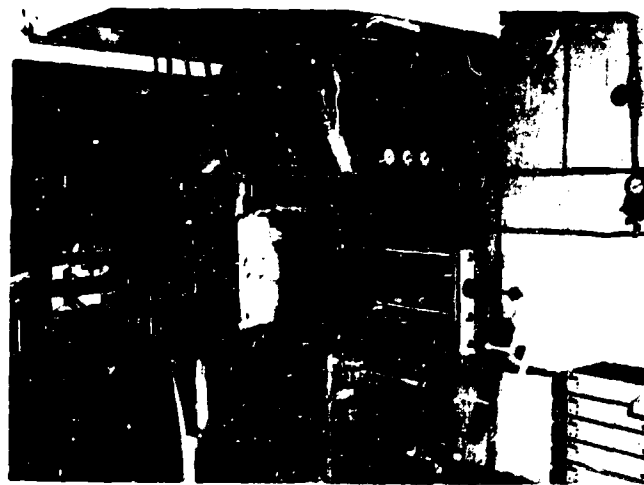


Figure 2. - OSU-HRR calorimeter.

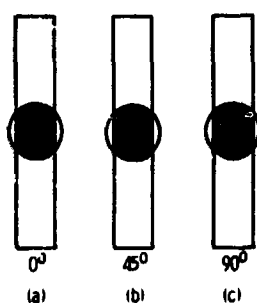


Figure 3. - Graphite fiber orientation. Circles represent flame coverage.

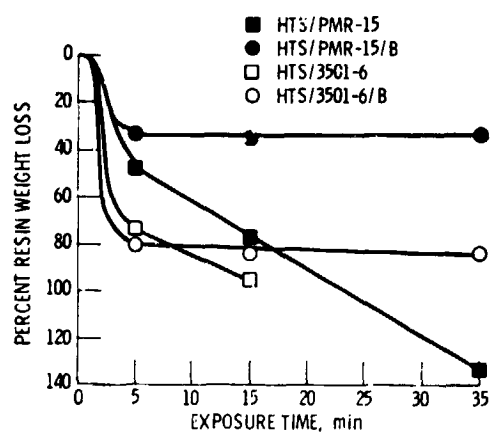


Figure 4. - Resin weight loss of laminates during exposure to 5, 3 Btu/ft²-sec thermal radiation in air in OSU-HRR calorimeter.



(a) UNFILLED.



(b) BORON FILLED.

Figure 5. - Surfaces of graphite/epoxy composite laminates burned in air by 5.3 Btu/ft²-sec radiation flux.

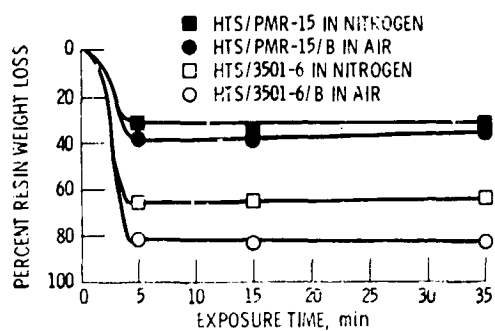


Figure 6. - Resin weight loss of laminates during exposure to 5.3 Btu/ft²-sec thermal radiation in OSU-HRR calorimeter.

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